

KECK GEOLOGY CONSORTIUM

PROCEEDINGS OF THE TWENTY-FOURTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

April 2011
Union College, Schenectady, NY

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ISSN# 1528-7491

The Consortium Colleges

The National Science Foundation

ExxonMobil Corporation

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2010-2011 PROJECTS

FORMATION OF BASEMENT-INVOLVED FORELAND ARCHES: INTEGRATED STRUCTURAL AND SEISMOLOGICAL RESEARCH IN THE BIGHORN MOUNTAINS, WYOMING

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EXPLORING THE PROTEROZOIC BIG SKY OROGENY IN SOUTHWEST MONTANA

Faculty: *TEKLA A. HARMS*, *JOHN T. CHENEY*, Amherst College, *JOHN BRADY*, Smith College

Students: *JESSE DAVENPORT*, College of Wooster, *KRISTINA DOYLE*, Amherst College, *B. PARKER HAYNES*, University of North Carolina - Chapel Hill, *DANIELLE LERNER*, Mount Holyoke College, *CALEB O. LUCY*, Williams College, *ALIANORA WALKER*, Smith College.

INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT, FRONT RANGE, COLORADO

Faculty: *DAVID P. DETHIER*, Williams College, *WILL OUIMET*, University of Connecticut

Students: *ERIN CAMP*, Amherst College, *EVAN N. DETHIER*, Williams College, *HAYLEY CORSON-RIKERT*, Wesleyan University, *KEITH M. KANTACK*, Williams College, *ELLEN M. MALEY*, Smith College, *JAMES A. MCCARTHY*, Williams College, *COREY SHIRCLIFF*, Beloit College, *KATHLEEN WARRELL*, Georgia Tech University, *CIANNA E. WYSHNYSZKY*, Amherst College.

SEDIMENT DYNAMICS & ENVIRONMENTS IN THE LOWER CONNECTICUT RIVER

Faculty: *SUZANNE O'CONNELL*, Wesleyan University

Students: *LYNN M. GEIGER*, Wellesley College, *KARA JACOBACCI*, University of Massachusetts (Amherst), *GABRIEL ROMERO*, Pomona College.

GEOMORPHIC AND PALEOENVIRONMENTAL CHANGE IN GLACIER NATIONAL PARK, MONTANA, U.S.A.

Faculty: *KELLY MACGREGOR*, Macalester College, *CATHERINE RIIHIMAKI*, Drew University, *AMY MYRBO*, LacCore Lab, University of Minnesota, *KRISTINA BRADY*, LacCore Lab, University of Minnesota

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GEOLOGIC, GEOMORPHIC, AND ENVIRONMENTAL CHANGE AT THE NORTHERN TERMINATION OF THE LAKE HÖVSGÖL RIFT, MONGOLIA

Faculty: *KARL W. WEGMANN*, North Carolina State University, *TSALMAN AMGAA*, Mongolian University of Science and Technology, *KURT L. FRANKEL*, Georgia Institute of Technology, *ANDREW P. deWET*, Franklin & Marshall College, *AMGALAN BAYASAGALN*, Mongolian University of Science and Technology.

Students: *BRIANA BERKOWITZ*, Beloit College, *DAENA CHARLES*, Union College, *MELLISSA CROSS*, Colgate University, *JOHN MICHAELS*, North Carolina State University, *ERDENE BAYAR TSAGAANNARAN*, Mongolian University of Science and Technology, *BATTOGTOH DAMDINSUREN*, Mongolian University of Science and Technology, *DANIEL ROTHBERG*, Colorado College, *ESUGEI GANBOLD*, *ARANZAL ERDENE*, Mongolian University of Science and Technology, *AFSHAN SHAIKH*, Georgia Institute of Technology, *KRISTIN TADDEI*, Franklin and Marshall College, *GABRIELLE VANCE*, Whitman College, *ANDREW ZUZA*, Cornell University.

LATE PLEISTOCENE EDIFICE FAILURE AND SECTOR COLLAPSE OF VOLCÁN BARÚ, PANAMA

Faculty: *THOMAS GARDNER*, Trinity University, *KRISTIN MORELL*, Penn State University

Students: *SHANNON BRADY*, Union College. *LOGAN SCHUMACHER*, Pomona College, *HANNAH ZELLNER*, Trinity University.

KECK SIERRA: MAGMA-WALLROCK INTERACTIONS IN THE SEQUOIA REGION

Faculty: *JADE STAR LACKEY*, Pomona College, *STACIL LOEWY*, California State University-Bakersfield

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EOCENE TECTONIC EVOLUTION OF THE TETONS-ABSAROKA RANGES, WYOMING

Faculty: *JOHN CRADDOCK*, Macalester College, *DAVE MALONE*, Illinois State University

Students: *JESSE GEARY*, Macalester College, *KATHERINE KRAVITZ*, Smith College, *RAY MCGAUGHEY*, Carleton College.

Funding Provided by:
Keck Geology Consortium Member Institutions
The National Science Foundation Grant NSF-REU 1005122
ExxonMobil Corporation

**Keck Geology Consortium: Projects 2010-2011
Short Contributions— Front Range, CO**

**INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT,
FRONT RANGE, COLORADO**

Project Faculty: DAVID P. DETHIER: Williams College, WILL OUMET: University of Connecticut

CORING A 12KYR SPHAGNUM PEAT BOG: A SEARCH FOR MERCURY AND ITS IMPLICATIONS

ERIN CAMP, Amherst College

Research Advisor: Anna Martini

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EVAN N. DETHIER, Williams College

Research Advisor: David P. Dethier

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HAYLEY CORSON-RIKERT, Wesleyan University

Research Advisor: Timothy Ku

RECONSTRUCTING THE PINEDALE GLACIATION, GREEN LAKES VALLEY, COLORADO

KEITH M. KANTACK, Williams College

Research Advisor: David P. Dethier

**CHARACTERIZATION OF TRACE METAL CONCENTRATIONS AND MINING LEGACY IN SOILS,
BOULDER COUNTY, COLORADO**

ELLEN M. MALEY, Smith College

Research Advisor: Amy L. Rhodes

**ASSESSING EOLIAN CONTRIBUTIONS TO SOILS IN THE BOULDER CREEK CATCHMENT,
COLORADO**

JAMES A. MCCARTHY, Williams College

Research Advisor: David P. Dethier

**USING POLLEN TO UNDERSTAND QUATERNARY PALEOENVIRONMENTS IN BETASSO GULCH,
COLORADO**

COREY SHIRCLIFF, Beloit College

Research Advisor: Carl Mendelson

STREAM TERRACES IN THE CRITICAL ZONE – LOWER GORDON GULCH, COLORADO

KATHLEEN WARRELL, Georgia Tech

Research Advisor: Kurt Frankel

**METEORIC ¹⁰BE IN GORDON GULCH SOILS: IMPLICATIONS FOR HILLSLOPE PROCESSES AND
DEVELOPMENT**

CIANNA E. WYSHNYSZKY, Amherst College

Research Advisor: Will Ouimet and Peter Crowley

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CHARACTERIZATION OF TRACE METAL CONCENTRATIONS AND MINING LEGACY IN SOILS, BOULDER COUNTY, COLORADO

ELLEN M. MALEY, Smith College
Research Advisor: Amy L. Rhodes

INTRODUCTION

The Boulder Creek Critical Zone Observatory (CZO) is located in an area steeped in mineral exploitation dating back to the 1880s. The Colorado Mineral Belt is comprised of igneous intrusions and ore deposits from the Laramide orogeny. This band strikes north-east/southwest through the region, stretching 250 miles (Tweto and Sims, 1963). Beginning in the late 1800s, this region was mined for gold, tungsten, lead, silver, and zinc (Fig. 1). Along with prospecting, mining, and smelting, this region was subject to deforestation and development with the flux of settlers in the late 1800s (Veblen and Lorenz, 1991). The surge of European settlers in the mining boom made this region an industrial hub, utilizing processes now known to have negative impacts on ecosystems.

The Boulder Creek CZO project focuses on the balance between natural weathering and erosion processes in the critical zone. The purpose of this investigation is to quantify heavy metal concentrations in regional soils to identify possible contamination associated with mineral exploitation. In investigation of soil processes in the critical zone, environmental impacts associated with the flux of human settlers, such as deforestation, road construction, and mining, should not be overlooked. In the case of mining, Diawara et al. (2006) report surface soil contamination of lead (300 ppm), arsenic (30 ppm), cadmium (5 ppm), and mercury (200 ppb) around major smelting sites in southern Colorado. While certain elements, such as Pb, have been detected in Boulder County soils, the heavy metal signature associated with this region has not been investigated in detail (Dethier, personal communication). This investigation characterizes the regional extent of metal contamination across a range of sites in Boulder County.

This investigation employs the analysis of spatial and

geochemical data to determine whether surface soils exhibit trace metal enrichment and, if so, to characterize the nature of contamination across southwestern Boulder County. This study investigates lead, arsenic, cadmium, chromium, barium, manganese, mercury, copper, iron, and aluminum. These 10 metals include major soil constituents (Fe, Al, Mn) and common environmental contaminants (Pb, Cd, As and Hg).

Trace metal enrichment in the A horizon compared to material from depth (C horizon) is expected to be a function of two variables: natural accumulation and external accumulation. Pedogenesis releases mineral-bound elements to the soil through weathering. Biochemical processes draw elements, such as manganese, from depth and concentrate them in surface soils via decomposition. Natural accumulation depends on profile weathering and organic enrichment.

Alternatively, external accumulation reflects anthropogenic deposition. The main control on deposition is the distance between a location and its potential contamination source, in this case, mining/smelting sites. The likelihood of contamination surrounding historic mining and smelting sites is based on the observation by Kabata-Pendias (2001) that metal halos surround locations such as these. With no other factors considered, metals associated with mining should be highest in concentration in soils surrounding the source of enrichment, and will decrease along a gradient with distance from the source, mostly in the direction of transport.

Controls on accumulation pertain to the affinity each soil has for an element. Kabata-Pendias (2001) suggests that organic and clay content are the main controls for metal adsorption in soils, as oxide minerals and organics have partial negative-charged surfaces, which tend to form weak bonds with positively charged metals. Soil pH affects metal solubility and

is a function of mineralogy and organic content. Eh/pH plots for elements demonstrate increased mobility in acidic, reducing soils. To characterize the distribution of metals in Boulder County soils in this investigation, trace metal concentrations were evaluated in relation to the soil properties of pH, % organic content, and % fine-grained material. Possible spatial relationships between trace metal concentrations and locations of mining and smelting locations were also investigated.

METHODS

To obtain a regional spectrum of soils, samples were collected along an east-trending elevation gradient from alpine (3450 m) to lower montane (1850 m) elevations; samples included three Boulder CZO sites: Green Lakes Basin, Gordon Gulch, and Betasso Preserve. Accessible sites along major roads between CZO sites also were sampled to characterize the region in higher detail (Fig. 1). Surface soils, consisting of organic and A horizons, were sampled to ~20 cm depth. Unaltered parent material (C horizon) was sampled at >1 meter depth to compare surface soils with unweathered parent material geochemically.

Thirty-three air-dried samples were sieved to <2 mm (-1 ϕ) fraction for acid digestion using the SCL

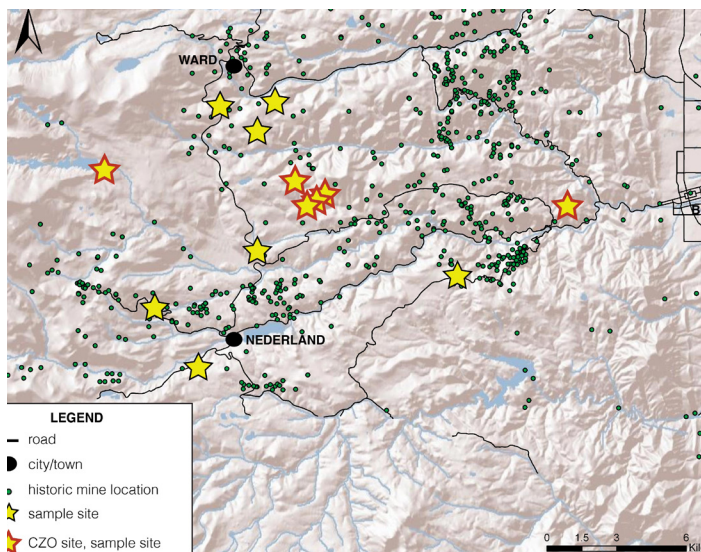


Figure 1. Map of southwestern Boulder County, Colorado showing sample sites and historic mine and smelter locations and towns, roads, and Boulder CZO sampling locations (Causey, 1998).

Method (Kimbrough, 1989). This method drives mineral- and organic-bound elements into solution using hot 4:1 concentrated HNO_3/HCl ('aqua regia'). This method is modified from EPA Method 3050B, which also leaches bioavailable elements and leaves mineral-bound elements undigested (USEPA, 1996).

The SCL Method yields primary and secondary filtrates for separate analysis. Extracts were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) for total Pb, Ba, Mn, Cu, Cr, Cd, Fe, and Al and graphite furnace atomic absorption spectroscopy (GF-AAS) for total As. Due to the rigorous, hazardous nature of SCL digestion, samples were selected for analysis based on location to maximize the spatial representation of analyses. Duplicate field samples and replicate extracts were used to ensure sampling and digestion precision.

Bulk analysis of total Hg using cold vapor atomic absorption spectroscopy (Hydra-C) was performed in the Environmental Geochemistry lab at Amherst College on sieved, oven-dried samples. Digestion was not required for this technique. Geochemical analyses of pH, organics, and partial grain-size were conducted using oven-dried <2 mm fraction to supplement metal data. pH was measured using 2:1 H_2O :soil slurries (Robertson et al., 1999). Percent organics were measured as loss on ignition (LOI), mass lost in ashing at 450 °C (Rowell, 1994). Partial grain-size analysis was performed to approximate percent clay-sized fraction. Geochemical data for each site were mapped in relation to historic mine locations using ArcGIS (Causey, 1998). Past and present production sites were incorporated into two sample parameters: distance from nearest mine site and mining density (number of historic sites within 1.5 km radius).

RESULTS AND DISCUSSION

Metals Results

Examination of trace metals in southwestern Boulder County soils compared with other physical and chemical soil properties ultimately allows for determination of whether soils have been impacted by mining activity and, if so, to what extent. Elemental concentrations obtained using ICP-OES, GFAAS,

and Hydra-C were normalized by soil digest mass. Results for As, Al, Ba, Cd, Cr, Cu, Fe, Mn, and Pb in mg/kg soil (ppm), and Hg in $\mu\text{g}/\text{kg}$ soil (ppb) are reported in Table 1. Sample concentrations were used to explore how metals fractionate, how metal concentrations vary by horizon, and how concentrations of one element relate to others within horizons.

Correlation ellipsoid matrices were used to generalize relationships between elements for each horizon. Corresponding elemental A and C horizon concentrations were compared to evaluate whether processes are occurring through the entire soil profile or are localized within a given horizon. Surface soil concentrations were analyzed spatially in relation to mining site locations using ArcGIS. Spatial parameters of distance to nearest mine site and number of mines within 1.5 kilometer radius for each sample site were created for statistical analysis, which is not addressed in this submission.

Examination of correlations between different trace metals and between trace metals and soil properties may provide insight regarding metal origin. For example, a correlation between two metals within the C horizon for all samples could suggest that the metal origin is similar and may be associated with parent material breakdown. Likewise, a strong correlation between two metals in surface soils and not at depth could suggest that the metals are derived from the same source, such as atmospheric deposition.

Fractionation of Elements

The finest material in soils is comprised of silt- and clay-sized mineral and organic particles, which bear a partial-negative surface charge and have high relative surface area (Kabata-Pendias, 2001). The charge and area draw metal cations to clay surfaces, which results in higher metal content in fine-grained fractions. In keeping with literature predictions about the behavior of trace metals in soils (Kabata-Pendias, 2001), fraction analysis of three samples showed higher trace metal concentration in fine-grained fractions (Fig. 2). Soil chemistry was comparable between $<63\mu\text{m}$ (silt/clay) and $63\text{--}125\mu\text{m}$ (very fine sand) fractions. Concentrations of fine fractions differed significantly from fractions $>125\mu\text{m}$.

For example, Pb and As show a negative correlation between grain-size and concentration (Fig. 2). Concentrations are higher in finer fractions than in coarse material for all elements. Analyses suggest that aluminum is lower in concentration at Magnolia Road, a 21 kyr moraine soil, compared to Gordon Gulch and Betasso sites. As this soil does not vary significantly in age with other sites (see Wyshnytsky, this volume), this difference is likely due to variations in host rock mineralogy between sites.

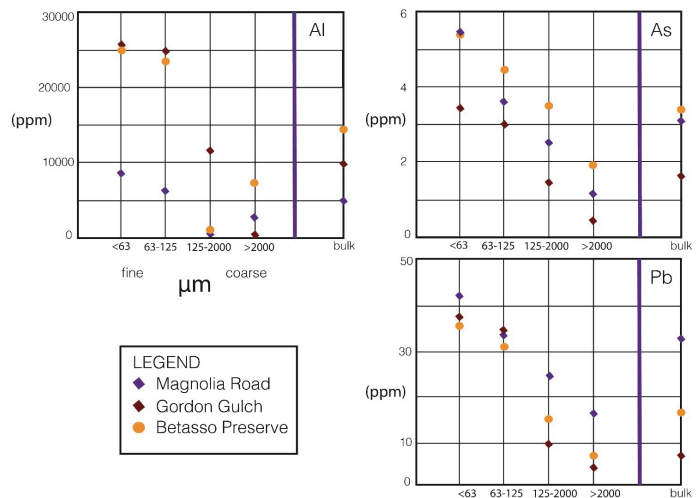


Figure 2. Example plots of Al, Pb, and As concentration distribution by size fraction (in μm) from three sample locations, compared with bulk concentrations in ppm (mg/kg soil) for each site.

Elemental Trends by Soil Horizon

Boulder County A horizons are enriched in Mn, Pb, Ba, Hg, and As. Surface soil enrichment results from accumulation and/or atmospheric deposition. Anthropogenic addition to soils from mining activity has occurred via atmospheric deposition. However, external dust input and bioaccumulation, the tendency for plants to draw elements from depth and concentrate them in surface soils, may also be occurring. Therefore, elements enriched at the surface may be of anthropogenic or natural origin. In contrast, C horizons are enriched in Cu and Cr. Iron and Al do not vary consistently between horizons. Elements without surface enrichment are likely derived from original host rock composition.

The A to C relationship across sites was evaluated by comparing elemental concentrations between A and

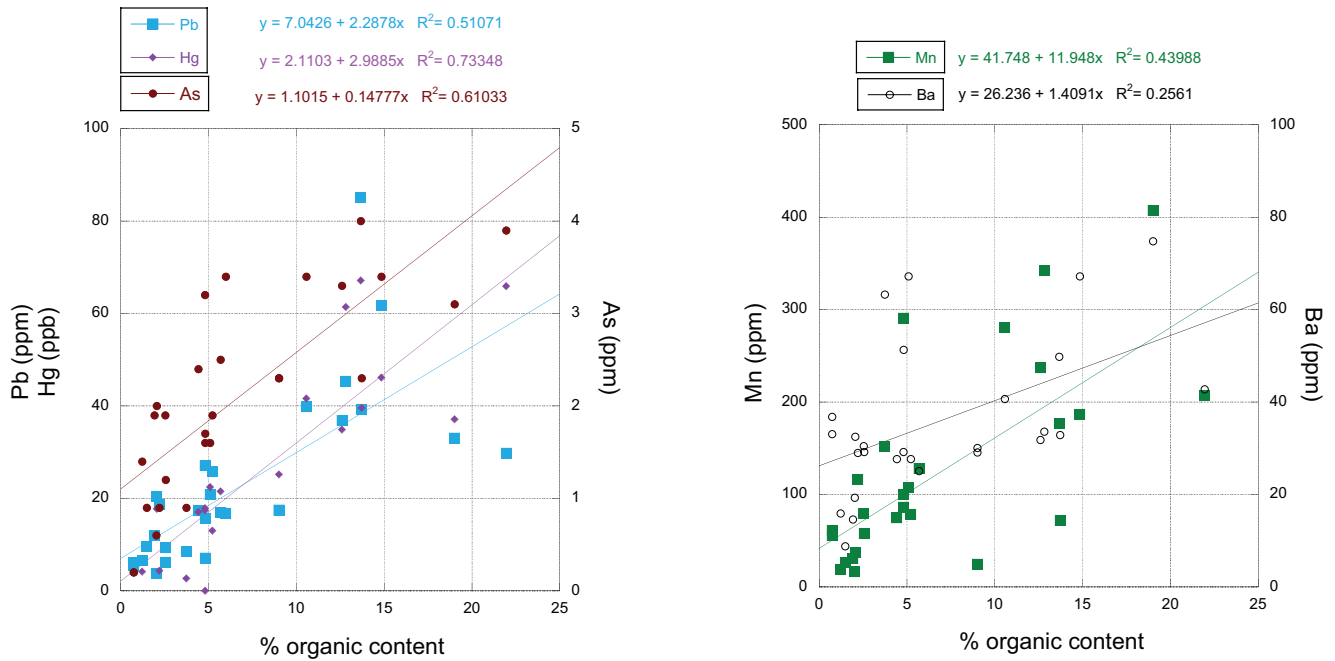


Figure 3. Mercury, As, Pb and Mn, Ba as functions of % organic content with regression line equations and associated R^2 values displayed. These correlations suggest that elements that are enriched in surface soils are associated with organic content.

C horizons collected at the same sample site. Linear trends between A and C horizons for Fe, Cu and Cr suggest that variations by site are associated with pedogenic breakdown of host rock. Enrichment in the A horizon and the relationships between A-enriched elements and soil properties, like % organics, warranted further investigation.

Elemental Relationships

In surface soils, enrichment of elements can be derived from natural and anthropogenic processes. Elevated concentrations of Mn and Ba may result from biological surficial concentration of elements from depth or from atmospheric dust input, while the source of Pb, As and Hg is anthropogenic (Kabata-Pendias, 2001). As Mn is extracted from depth over time by plants, decomposing organic matter may concentrate Mn in surface soils (Kabata-Pendias, 2001). There is a positive correlation between Mn and Ba, which suggests a common source. Mercury, Pb, As, Mn, and Ba are enriched in surface soils, and each has a positive correlation with % organic content (Fig. 3).

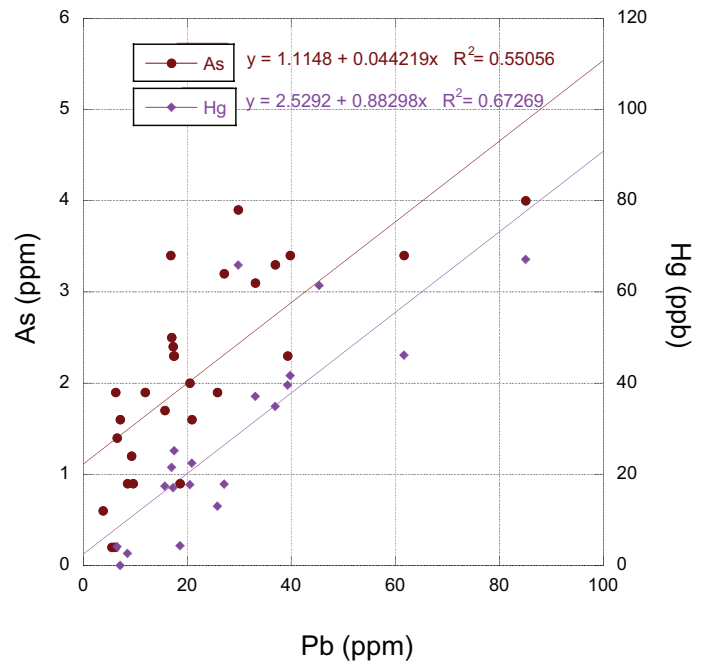


Figure 4. Mercury (ppb) and As (ppm) across all horizons and sites with corresponding Pb (ppm) concentrations, showing the relationship between Hg/Pb and As/Pb across southwestern Boulder County. R^2 values (Hg/Pb $R^2 = 0.67$, As/Pb $R^2 = 0.55$) suggest correlation between variables.

The most striking trend in trace metals occurs between Pb, As, and Hg in surface soils (Fig. 4). Strong correlation between Pb, As, and Hg (Fig. 4) in surface soils suggests that these metals were deposited via a common atmospheric anthropogenic source.

In the C horizon, Fe and Mn, Fe and Al, and Fe and Cr are positively correlated, suggesting that these elements are associated with host rock breakdown. No relationship between Cu and Cr exists, though both of these elements are enriched at depth. The positive correlations between Cr and Fe and Cr and Al suggest that chromium is present in host rock, and it was incorporated into soils by pedogenesis. Iron and Mn are positively correlated at depth, but not in surface soils where Mn is enriched. This difference could be attributed to Mn-rich dust inputs or bioaccumulation in organic matter (Kabata-Pendias, 2001).

Mining Signal and Implications

Surface soils are enriched with respect to Mn, Ba, As, and Pb, but not all A horizon enrichment can be attributed to anthropogenic activity. Barium and Mn have a weak association with organic content, and these elements may be enriched due to bioaccumulation (Kabata-Pendias, 2001). The correlation between As, Hg, and Pb in surface soils suggests that these metals are affiliated with atmospheric deposition. These metals are associated with ore smelting processes that may have been used in the Boulder County region (Kabata-Pendias, 2001). These trace metal signatures are likely evidence of the mining legacy in the region.

CONCLUSIONS

The enrichment of surface soils in elements associated with anthropogenic activity suggests that Boulder County soils bear a signature associated with historic mining activity in the region. Surface soils in southern Boulder County are enriched in Hg, Mn, Ba, As, and Pb. Lead, arsenic, and mercury enrichment likely results from anthropogenic atmospheric inputs from mining activity, whereas the origin of manganese and barium enrichment is likely from bioaccumulation or dust inputs. Measured concentrations of metals reflect mechanisms of deposition and mobilization. While other elements may have been associated with

deposition, Pb, As, and Hg are potential contaminants with a related source. This investigation of potential contamination of toxic elements bears significance for the Boulder Creek watershed, as the heavy metals in surface soils are bioavailable (U.S. EPA, 1996) and could mobilize. Further exploration will quantify the mass of each element by area to characterize contamination potential of the watershed.

Within a soil profile, trace metals form weak bonds with fine-grained (<125 μm) soil material. There is no correlation between % fine-grained particles and total metal content. More exploration and detailed grain-size analysis is required to further characterize this relationship. Ranges of trace elements across southern Boulder County do not exceed the ambient ranges reported by Kabata-Pendias (2001) for the United States, as indicated in Table 1. Detailed sampling of soils for geochemistry near known, historic mining and smelting sites could more thoroughly characterize the processes governing trace element accumulation and mobility.

ACKNOWLEDGEMENTS

Many thanks to Dr. David Dethier, Dr. Will Ouimet, and the Keck soil crew for their unlimited muscle and brainpower. I would like to thank my adviser, Dr. Amy Rhodes, for her guidance and assistance with

Element	O (n=7)	A (n=16)	C (n=10)	U.S. Average ^C
Al (ppm)	4000 – 14000	11000 – 29000	16000 – 32000	up to 10%
Fe (ppm)	7000 – 25000	18000 – 24000	17000 – 24000	0.5 to 5%
Mn (ppm)	6 – 300	80 – 320	20 – 80	400 - 600
Ba (ppm)	7 – 27	21 – 87	16 – 34	~600
Cr (ppm)	5 – 25	20 – 48	24 – 64	40 - 55
Cu (ppm)	6 – 22	6 – 16	6 – 26	26
Pb (ppm)	10 – 50 ^A	10 – 50	4 – 16	17 - 26
As (ppm)	1 – 3	2 – 4	0.4 – 1.8	5 - 7
Cd (ppm)	0.3 – 1.2	0.7 – 1.3	0.5 – 1.1	0.3 - 0.5
Hg (ppb) ^B	51 – 141	12 – 53	4 – 18	60 - 170

Table 1. Table of normalized concentrations from ICP-OES (Al, Ba, Cd, Cr, Cu, Fe, Mn, Pb), GFAAS (As), and cold vapor atomic absorption spectroscopy (Hg). Values reported represent $\mu \pm 1\sigma$. A: anomalous >1000 ppm sample excluded from range (n=6); B: O (n=4), A (n=14), C (n=3). C: compared with mean values in U.S. soils, as reported by Kabata-Pendias (2001).

this project. I also thank Dr. Robert Newton, for his encouragement and wisdom, and Dr. Anna Martini and Erin Camp at Amherst College for their assistance with mercury analysis.

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